The Synthesis and Characterization of Substituted Phosphates and Layered Manganese Oxides

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Project ID #
ES050

Overview

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Timeline

- Project start date: 06-01-2008
- Project end date: 12-31-2011
- Percent complete: 90%

Budget

- Total project funding
  - DOE share: 100% $
  - Contractor share: Personnel
- Funding received
  - FY10: 294k$
  - FT11: 340k$

Barriers

- Barriers addressed
  - Lower-cost,
  - Higher power,
  - Higher capacity and
  - Abuse-tolerant safer cathodes

Partners

- MIT, SUNY Stony Brook, LBNL, BNL, NREL, ORNL, PNNL, Georgia Tech.
- Primet, and other companies

Objectives and Relevance of Work

- The primary objectives of our work are to find:
  - Lower-cost and higher capacity cathodes, exceeding **200 Ah/kg** (700-800 Wh/kg - lab theoretical).
  - Moderate rate PHEV compatible cathodes
  - Both of the above are to be based on environmentally benign materials

Relevance: Milestones

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a) Determine the optimum composition of $LiNi_yMn_yCo_{1-2y}O_2$ for PHEV applications (Sept. 10)

- **$LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ is optimum of stoichiometric $LiMO_2$.**

b) Identify $LiNi_yMn_yCo_{1-2y}O_2$ systems that can achieve 200 Ah/kg for PHEV applications (Mar. 11)

- **200 Ah/kg will be hard to attain without new electrolytes, without going lithium-rich, and then the desired rate may not be attained.**

c) Identify and evaluate phosphate structures, containing Fe and/or Mn, that have the potential of achieving an energy density exceeding 700 Wh/kg. (Sep. 11)

- **Ongoing, with some promising leads**

d) Identify other materials, including those containing vanadium, that can undergo more than one electron transfer per redox center (Sep. 11)

- **Identified several transition metal elements that can undergo more than one electron transfer**

Approach and Strategy: Improved Cathodes

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- Place emphasis on low cost materials,
  - Synthesize by practical approaches
  - Structurally characterize, including defects and morphology
  - Electrochemically evaluate in a range of cell configurations

  - Transition metal layered dioxides
    - Minimize expensive components, such as cobalt.
    - Determine inherent rate capability.
    - Determine maximum lithium capacity, and relate to charging voltage.
    - Answer the question: Can 200 Ah/kg be obtained for $LiMO_2$ at $\geq$ 1C rate?
      - Unlikely that this milestone can be accomplished with today's electrolytes

  - High capacity transition metal phosphates
    - Systematic doping of olivine – understand role of V in $LiFePO_4$.
      - V substitutes for iron and enhances rate (Milestone complete)
    - Explore non-olivine phosphates and related materials.
      - Iron pyrophosphates cycle – better electrolyte needed (Milestone)

Technical Accomplishments:
Barriers being Addressed

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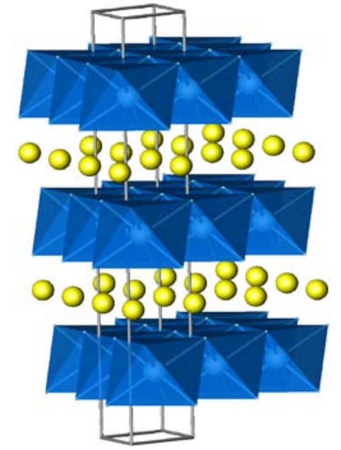
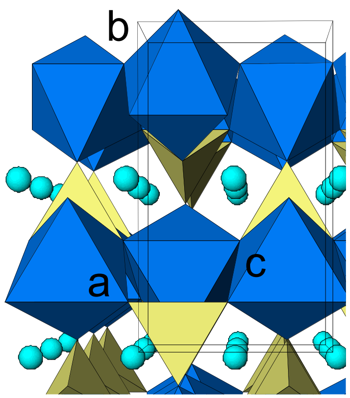
Lower-cost, higher power, higher-capacity and abuse-tolerant safer cathodes

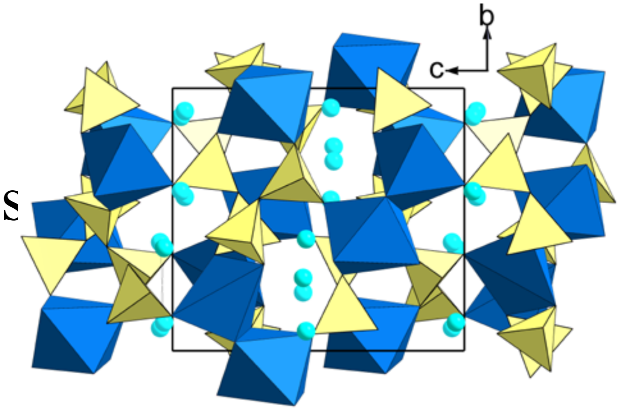


- Ultimate capability of the MnO_2 and NiO_2 lattice
  - Can capacity be increased to 200 Ah/kg at C rate is?
    - Must cell voltage be reduced to increase capacity?
  - Why is the rate capability lower than that of olivine?



- Olivines
  - What is role of substitutes in lattice
    - **Can vanadium be placed in the lattice?**

- Beyond Olivines
  - > 200 Ah/kg from phosphate-type structures
    - Must vanadium be involved?
  - The stability of high voltage cathodes - electrolytes



Status of $LiMO_2$ in 2010

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- What is maximum Mn in $Li(Ni_yMn_zCo_{1-y-z})O_2$?
  - Maximum Mn is 0.5 in lithium stoichiometric material
    - Electrochemistry is good, but lower rate than $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
  - Rate suffers for Mn > 0.5 in lithium-rich materials
- What is actual capacity for $LiNi_yMn_yCo_{1-2y}O_2$?
  - 180 Ah/kg for a 4.3 volt cut-off on charging
  - 200 Ah/kg for a 4.4 volt cut-off on charging
    - But, all cells show a 1^{st} cycle loss of 10-15 Ah/kg
    - Thus, theoretical capacity of over 220 Ah/kg needed for 200 Ah/kg practical
  - Can 200 Ah/kg be achieved with present electrolytes?
  - In last 12 months addressed the following questions
    - What is limiting capacity?
    - What is limiting power capability?
    - Work with high-voltage cathode team to use and high voltage electrolytes
    - Do we have to go to lithium-rich and find a way for improving rate?

Co impacts Theoretical Capacity of $LiNi_yMn_yCo_{1-2y}O_2$

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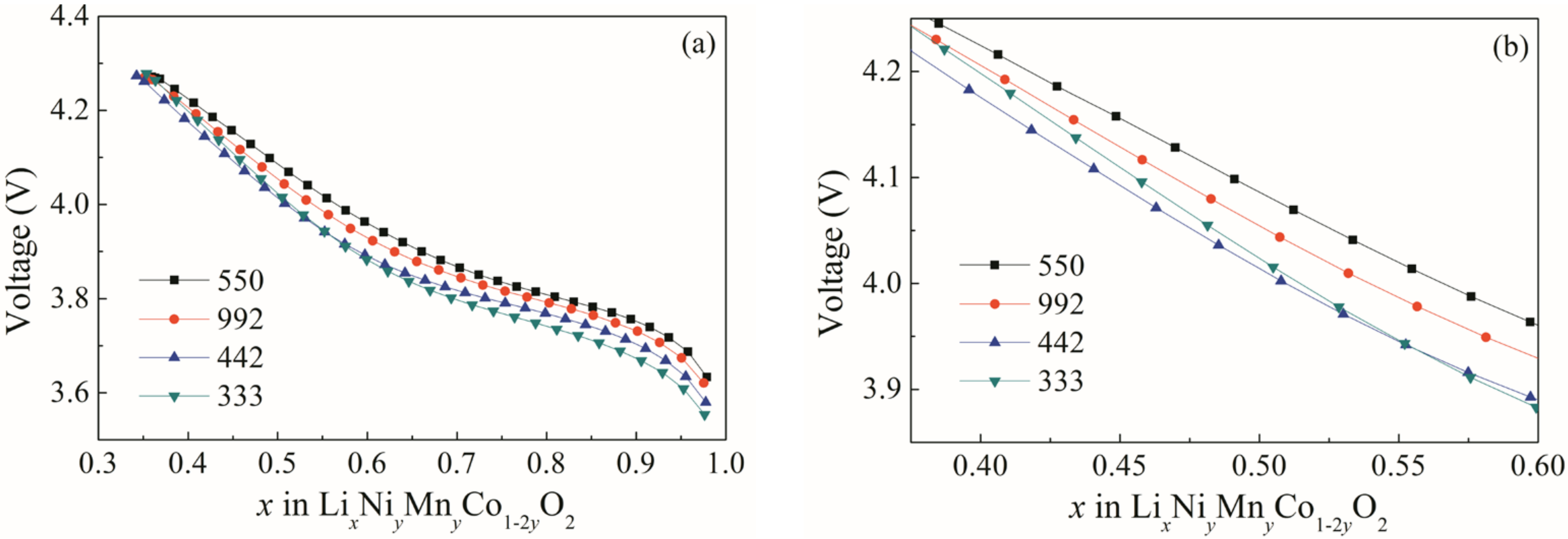
- Cross-over effect of Cobalt:
  - Cobalt causes a more rapid increase of open circuit voltage on charging
    - Voltage increases above that of Li_x442 at x = 0.55
    - Voltage increases above that of Li_x992 at x = 0.38
  - Increase of cobalt content reduces capacity to a given cut-off voltage



$LiNi_yMn_yCo_{1-2y}O_2$ has High Power Capability

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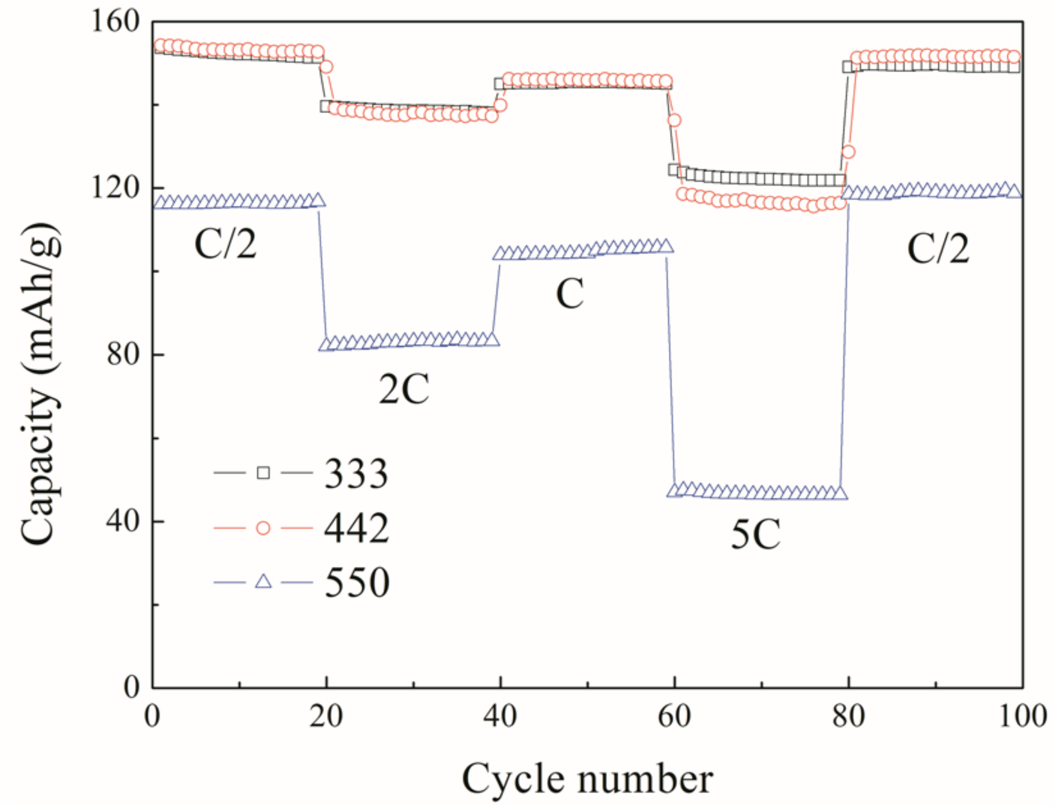
- Binder-free test of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
  - Shows high rate capability, comparable to that of 333 composition
  - Much superior to cobalt free 550 composition
- Thus, material has inherent power capability

Binghamton Material

Tested at NREL by C. Ban and A. Dillon



Are Lithium-Rich Layered Oxides Superior to the Stoichiometric Materials?

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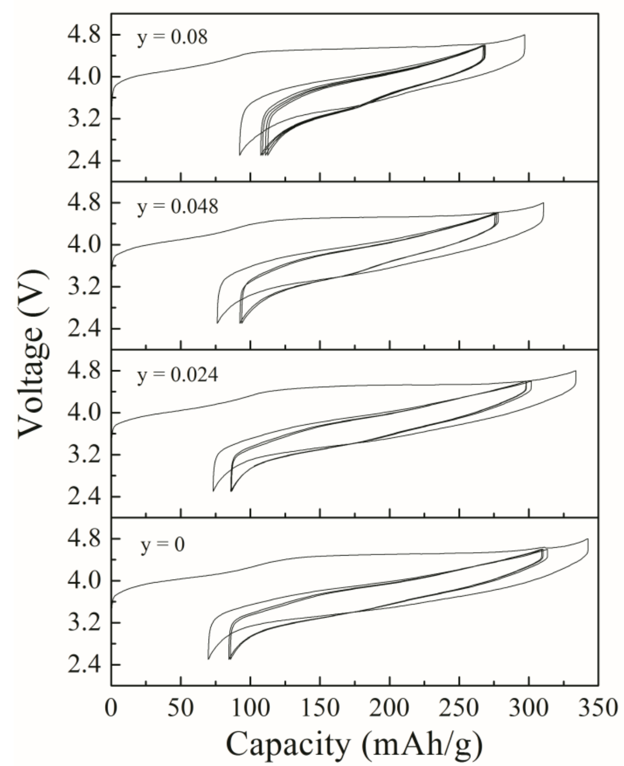
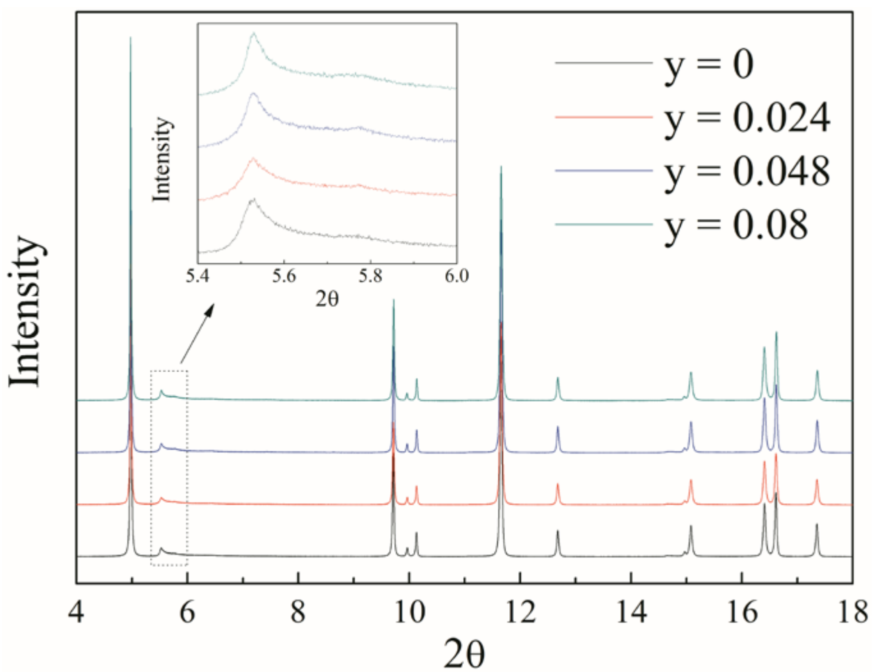
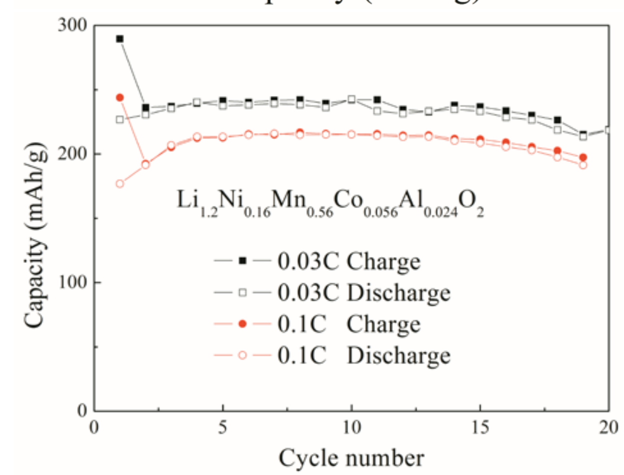
- Al substituted Lithium-rich materials increase the capacity and lower the cost
  - Solid solution $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08-y}Al_yO_2$ (high resolution XRD) have more than 200 Ah/kg capacity (2.5V-4.8V)
  - $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.056}Al_{0.024}O_2$ deliver around 200 Ah/kg capacity at 0.1C at room temperature
- Can Al substitution increase thermal stability?
  - preliminary data says yes
- Can power capability be improved? Maybe







Vanadium substitutes into $LiFePO_4$ giving higher capacity and rate

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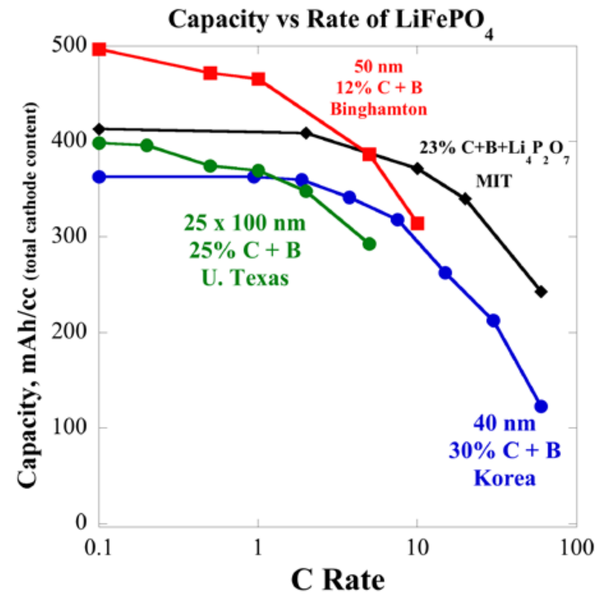
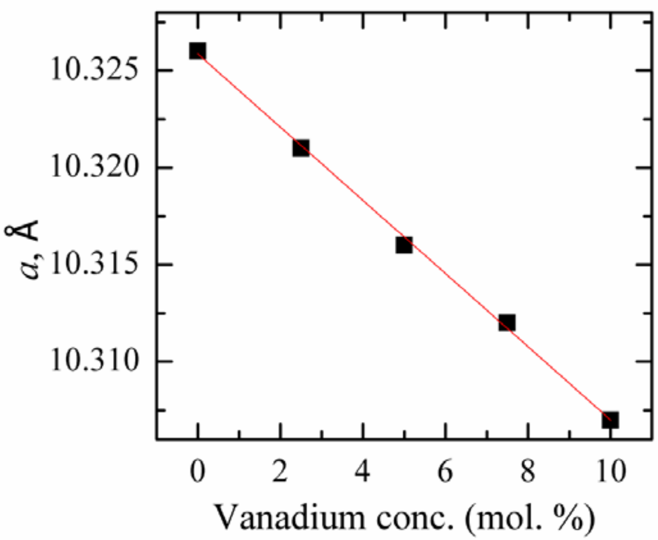
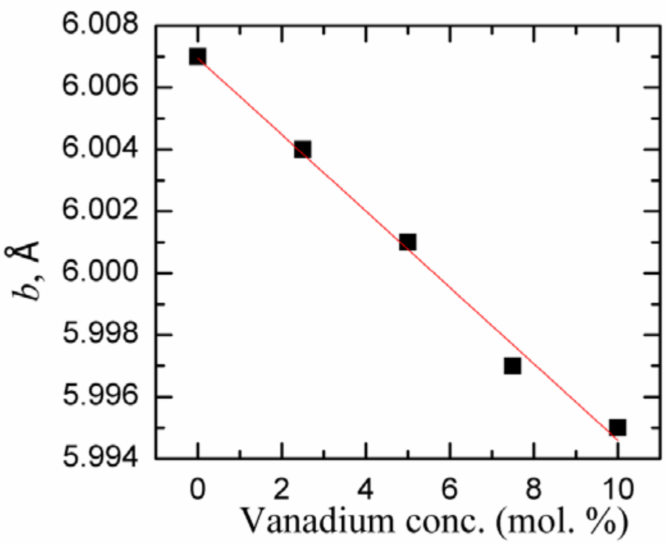
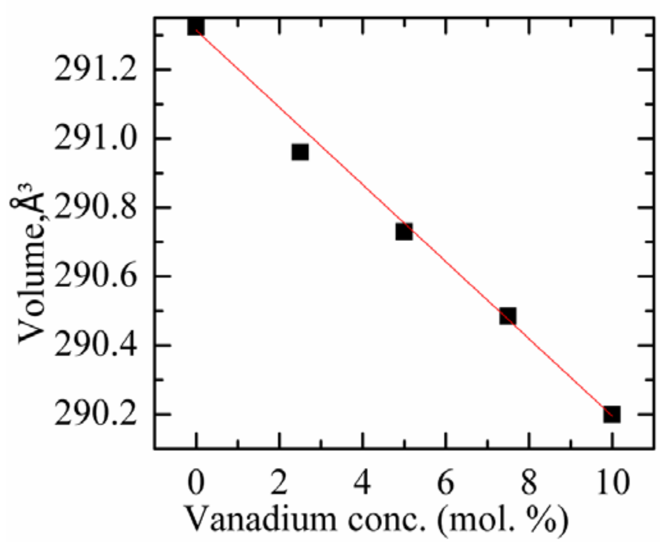
- Last year we showed that $LiFePO_4$ gives nanostructure with V
  - Gives highest volumetric capacity
- Last year's future work: does V go into lattice?
  - Vanadium goes on Fe site at 550°C
    - X-ray proves it up to 10% V
    - Vegard's solid solution law obeyed









Vanadium addition to $LiFePO_4$ gives higher capacity and rate

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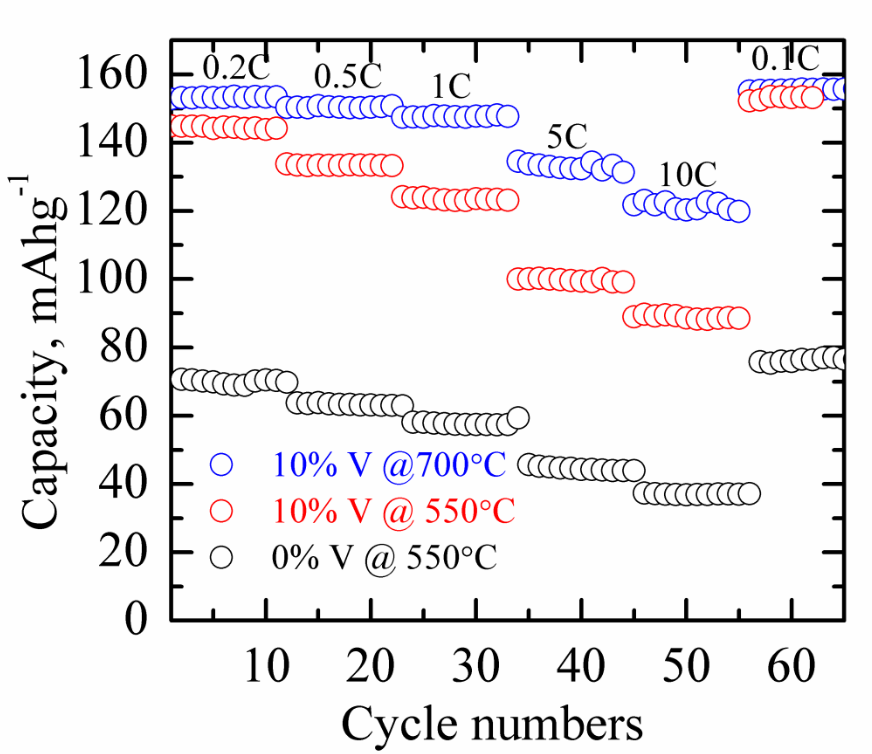
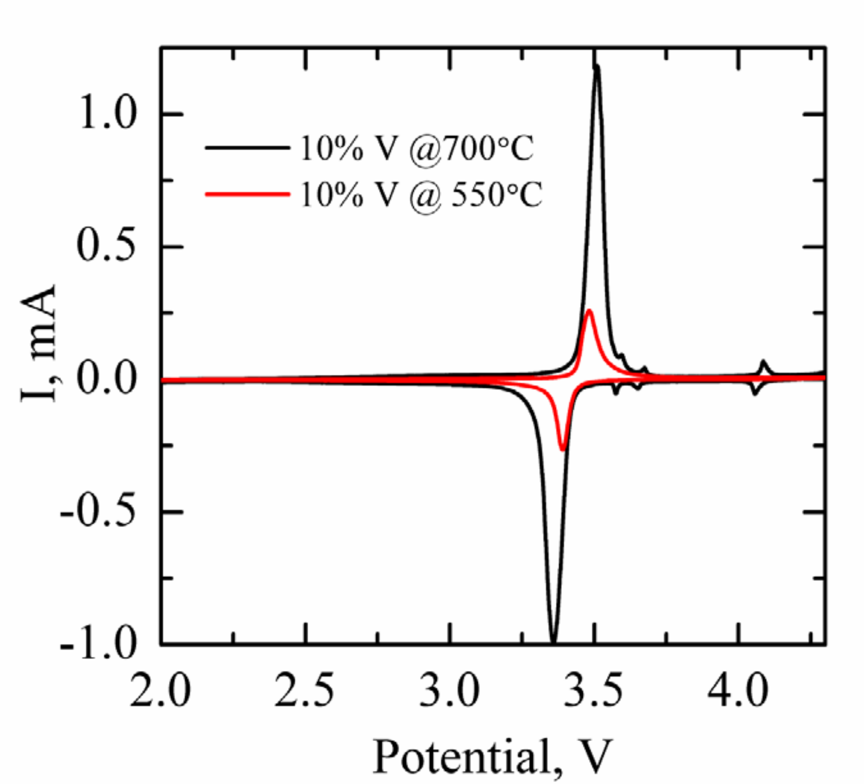
- BATT Project is now complete
  - Vanadium goes on Fe site at 550°C
    - X-ray proves it for at least 10% V
  - At 700°C some V rejected
    - $Li_3V_2(PO_4)_3$ formed
    - Shows best electrochemistry





200 Ah/kg or 700+ Wh/kg Cathodes

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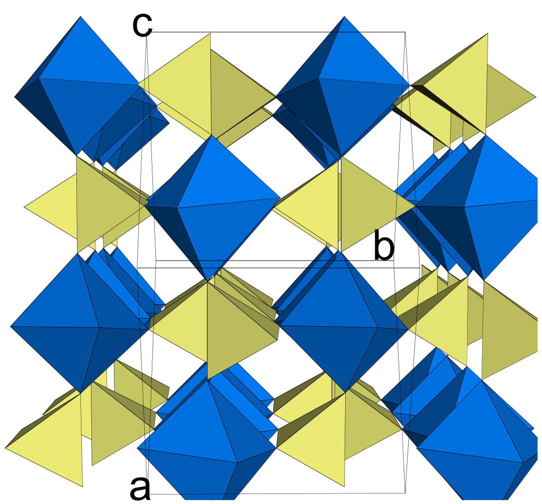
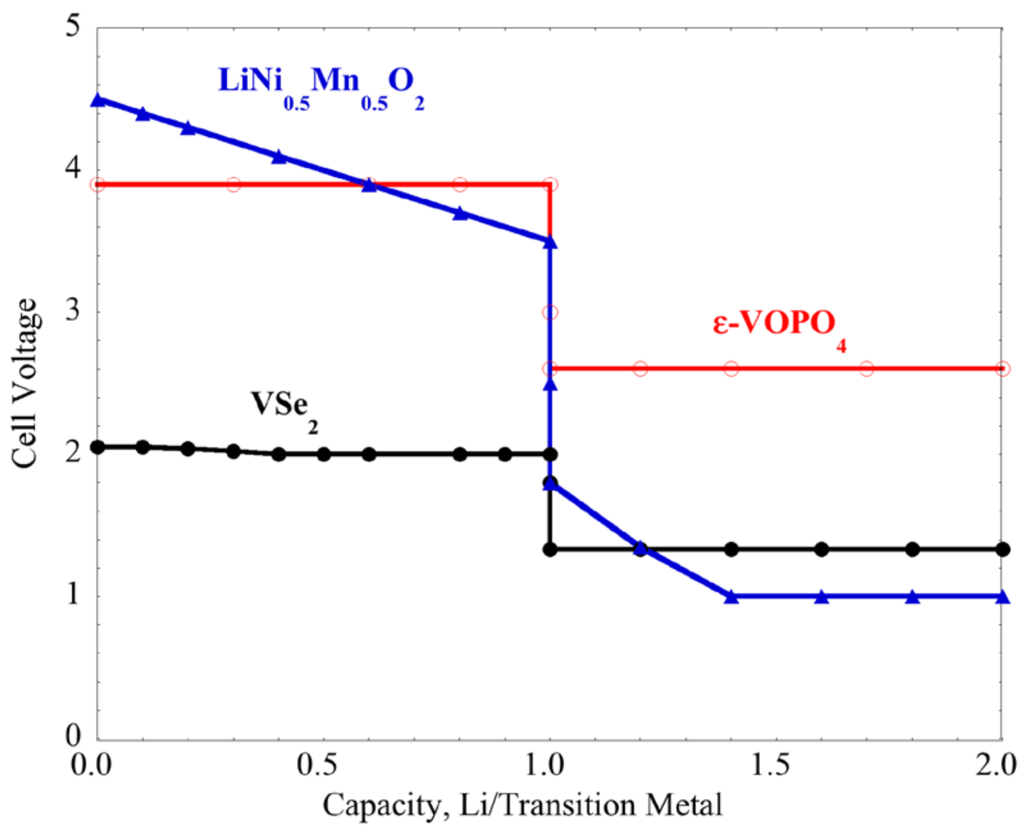
- Options
  - Several materials known to react with more than 1 lithium
    - Dc to dc converters can handle voltage differences
  - Higher voltage cathodes
    - Spinel, Li“Co”PO_4 (not cobalt)
  - Combination of above two
- Search for new structures





Higher Capacity Cathodes: >1 Li/M

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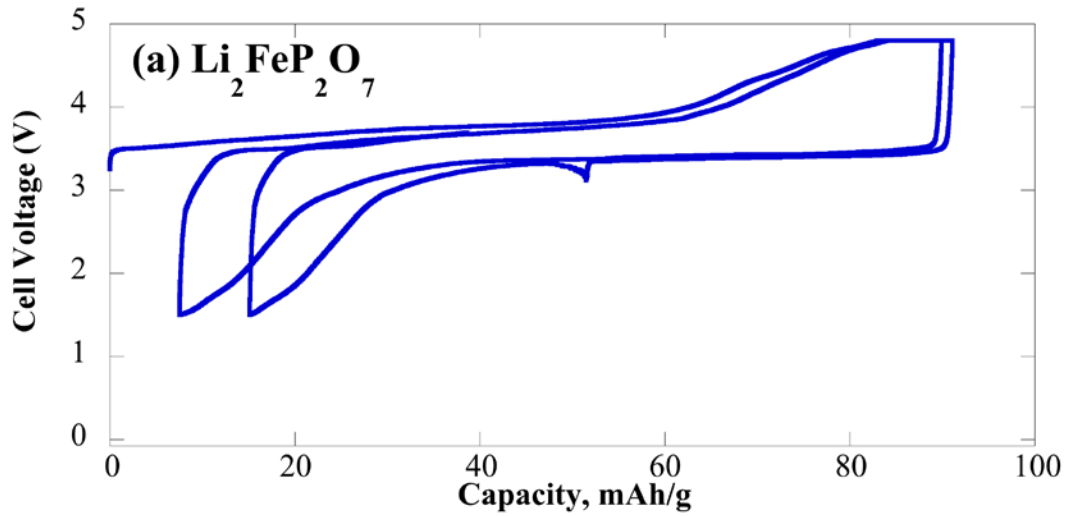
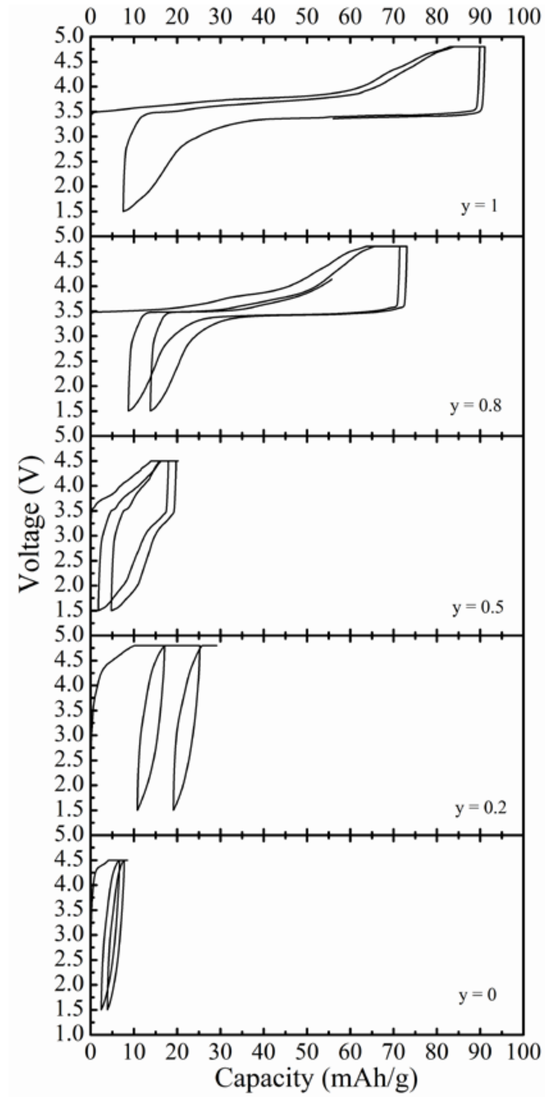
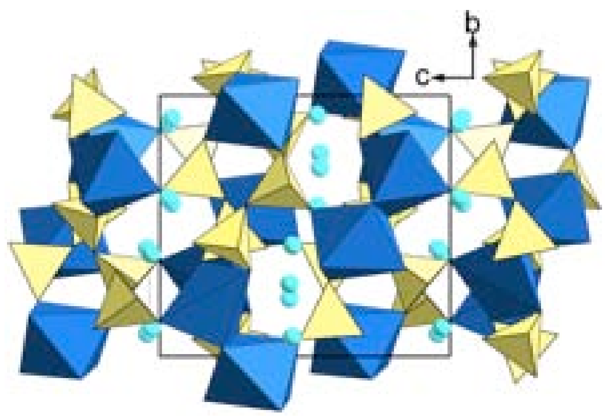
- Mn and Fe pyrophosphates
  - Status 2010
  - $Li_2(FeMn)P_2O_7$ formed for range of Fe and Mn
    - Capacity is directly related to Fe content





Structure now determined



Higher Capacity Cathodes: >1 Li/M

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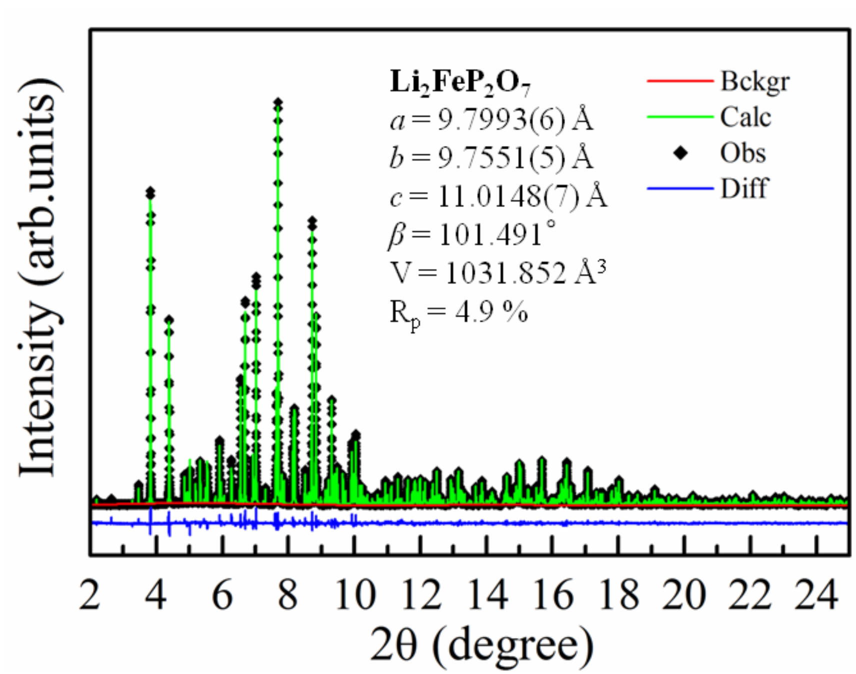
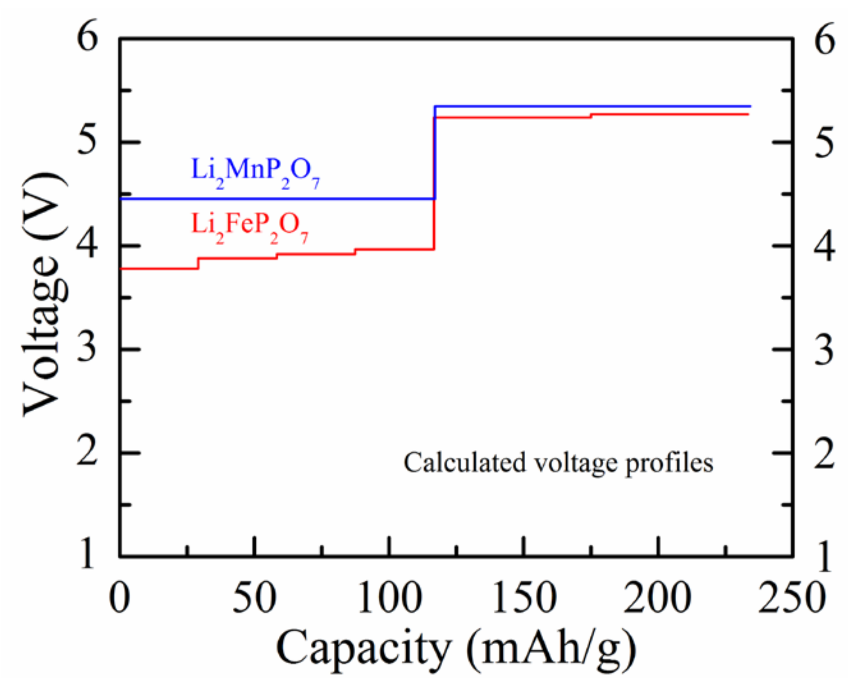
- Mn and Fe pyrophosphates
  - $Li_2(FeMn)P_2O_7$ formed for complete range of Fe and Mn
    - Structure determined using data from APS-ANL
    - Is it possible to remove 2nd lithium at higher voltage?
      - Ceder at MIT calculated redox potentials (BATT program)





Higher Capacity Cathodes: >1 Li/M

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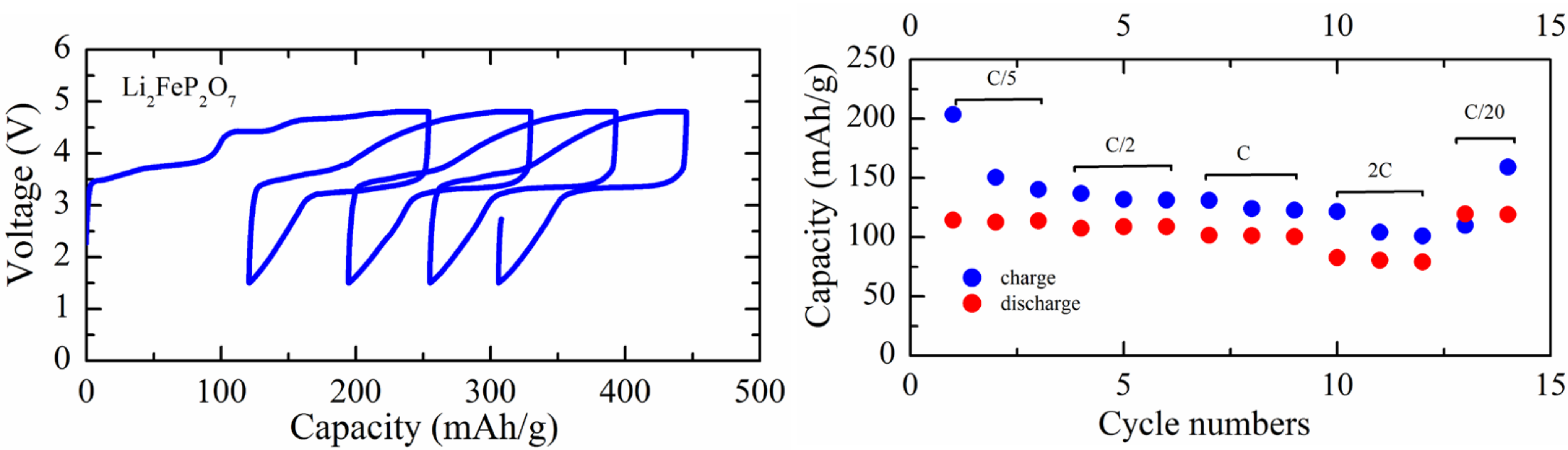
- Significant improvement on the performance after nano-scissoring (Primet collaboration)
  - Particle size reduced from microns to less than 100 nm
  - More than one lithium can be cycled
    - Maybe both lithium can be extracted with appropriate electrolyte
    - Good structural reversibility during the cycling



Collaboration and Coordination with other Institutions

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- **APS at ANL**
  - High resolution x-ray diffraction data for olivines, pyrophosphates and spinels.
- **G. Ceder at MIT** (BATT-VT funding)
  - Determination of redox potentials of Fe-Mn pyrophosphates, and other materials
    - Redox for 2nd Li at limit of electrolyte stability; published
- **Primet (Ithaca Co)**
  - Collaboration underway on nanosizing materials (Nano-scissoringTM)
    - Pyrophosphates, olivines, high voltage spinels (ARL-CERDEC)
  - Determination of redox potentials of Fe-Mn Pyrophosphates, and other materials
- **C. Ban and A. Dillon (NREL)**
  - High rate evaluation of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
    - 1st phase of collaboration showing high rate complete and published
- **F. Alamgir (Georgia Tech.)**
  - In-situ XAS measurements of LixMO2 at Brookhaven
    - Work complete showing role of cobalt in controlling voltage; in press
- **J. Cabana (LBNL-**BATT**), J. Xiao (PNNL), Primet**
  - Initial collaborations underway on high voltage spinels,

Future Work

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- **$LiMO_2$**
  - Complete work on layered oxides, $LiMO_{2,}$ 2Q 2011
    - Work with A. Dillon and C. Ban of NREL
- **High Capacity Phosphates and Related Structures (2 electron)**
  - Identify and evaluate phosphate structures, containing Fe and/or Mn, that have the potential of achieving an energy density exceeding 700 Wh/kg.
    - Complete studies on pyrophosphate
    - Explore structure retention of $VOPO_4$ lattice on cycling
- **Identify other materials, including those containing vanadium, that can undergo more than electron transfer per redox center**
- **High Voltage Cathodes**
  - Work with J. Cabana (LBNL), J. Xie (PNNL) and Primet on spinel
    - Collaborate with high voltage electrolyte group (also applicable to 2e phosphate

Summary

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- **$LiMO_2$** - $LiNi_{0.40}Mn_{0.40}Co_{0.20}O_2$ is optimum composition for Li/M = 1
  - Same rate capability as $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$
    - 200 Ah/kg will not be attained with present electrolytes
      - NOGO for 200 Ah/kg
      - GO for replacement of 333 NMC
    - Built collaboration with NREL – will use on other systems
- **Olivine** – $LiFePO_4$
  - Partial substitution of Fe is possible
    - Improves capacity and rate capability (GO)
- **Multiple electron** materials
  - Iron pyrophosphate characterized and lithium can be cycled
    - Challenge is getting 2nd lithium out
      - Working with G. Ceder at MIT on determining potentials
      - Working with Primet on nano-sizing the material
      - Working with high voltage electrolyte team/experts
- Technology transfer underway
  - Students in battery companies and at BNL, NREL and PNNL
  - Publications and presentations to transfer knowledge
    - NYBEST consortium